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STRONG, DURABLE ADHESIVE BONDING: SOME ASPECTS OF SURFACE PREPARATION, JOINT DESIGN AND ADHESIVE SELECTION

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Structural adhesive bonding offers a variety of advantages over mechanical fastening or welding as a method of construction.These advantages include a substantial weight saving, more uniform stress distribution over the joint area and sealing against moisture ingress. In order to realise those potential benefits particular attention must be paid to a number of factors, principally surface preparation of the materials to be joined, the design of the joint in relation to the type and level of stress to be encountered in service and the selection of the chemical class of the adhesive in relation to the environment in which it is to operate.

This paper explores a number of topics, including the wetting of a solid substrate by a liquid adhesive, the stress distribution in a loaded single lap joint and the cure cycle employed for an epoxy-based adhesive, by way of illustration of the importance of these factors on initial joint strength and on joint durability.

INTRODUCTION

Structural adhesive bonding has been in widespread use in critical aircraft applications for many years. In the aerospace industry the potential benefits offered by adhesive bonding by comparison with mechanical fastening as a method of joining, such as lighter weight and more uniform stress distribution, have long been recognised.

In spite of the extensive use in aerospace applications adhesive bonding has not made great inroads into other structural applications. This can be attributed, at least in part, to a lack of confidence arising from insufficient appreciation of the importance of certain fundamentals in adhesive bonding, most notably preparation of the surfaces to be joined, joint design in relation to the loading pattern to be encountered in service and adhesive selection having regard to the loads and environment associated with the proposed application. There is also, in some quarters, a view that adhesive bonding is an unskilled operation. Espousal of this view, and the attendant lack of attention to the above points, rapidly results in a low level of user confidence.

This paper considers various facets of surface preparation, joint design and adhesive selection and the contribution these make to the achievement of strong, durable adhesive joints for structural applications. It does not attempt to be an exhaustive discussion of these matters but rather draws attention to the wide range of factors which must be taken into account to achieve strong, durable bonds.

SURFACE PREPARATION

The object of surface preparation is to ensure that the weakest link in the whole assembly is not the level of adhesion at the adhesive/substrate interface, that is, when fracture occurs it is away from the interface and consists of a cohesive failure of substrate or adhesive rather than at the interface (adhesive failure) (Fig. 1). The selection of the surface preparation method for a given application depends on the type of materials to be joined and the nature of their surfaces and also on the environment and stress levels to be encountered in service.

Wetting

A necessary, but rarely sufficient, prerequisite for strong, durable adhesive bonding is good wetting of the substrate by the adhesive. To obtain strong bonding at the interface the formation of specific chemical bonds between substrate and adhesive

is not essential. Physical interaction (van der Waals forces) is potentially powerful but the strength diminishes rapidly with separation distance and intimate contact between the two phases is necessary. Similarly, to form covalent bonds across the interface close contact is needed. In addition, surfaces are not flat on a microscopic scale and intimate interfacial contact means a greatly increased area of interaction compared with the nominal, macroscopic area. Maximum advantage should be taken of this (Fig. 2) Failure to achieve complete wetting not only underutilises the bonding area available but also results in air pockets and bubbles along the interface, thereby forming regions of weakness in the joint.
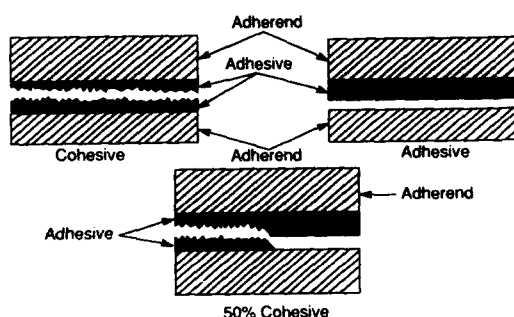

Figure 1 Schematic representation of cohesive and adhesive failure of a bonded joint. (After Cagle ref.1).
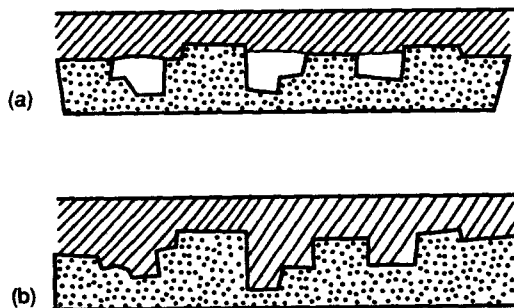

Figure 2 Schematic representation of incomplete and complete wetting of a solid substrate by a fluid adhesive. (After Minford, ref. 2).

The wetting and spreading of a liquid adhesive over a solid substrate has been extensively studied, building on and extending the original relationship established by Young and Dupre between the surface free energies of liquid and solid and the equilibrium contact angle adopted by the liquid on the solid. Complete wetting means a contact angle of zero. For spontaneous spreading the surface free energy (or more properly the critical surface tension of wetting) of the liquid should be less than that of the substrate.

Polymeric adhesives, such as epoxies, have surface free energies broadly around 45–50 mJm⁻². Many polymers have surface free-energies in the 30–45 mJm⁻² range[3]. For example for polyethylene the value is about 31 mJm⁻² and for the more polar PVC about 40 mJm⁻². Raising the surface free energy is than a matter of introducing more polar groups into the surface region and many surface preparation techniques are designed to do this via polymer oxidation. Corona discharge treatment of polyethylene film for improved print adhesion is an example of this[4]. The beneficial effects on adhesive joint strength are illustrated in Fig 3.

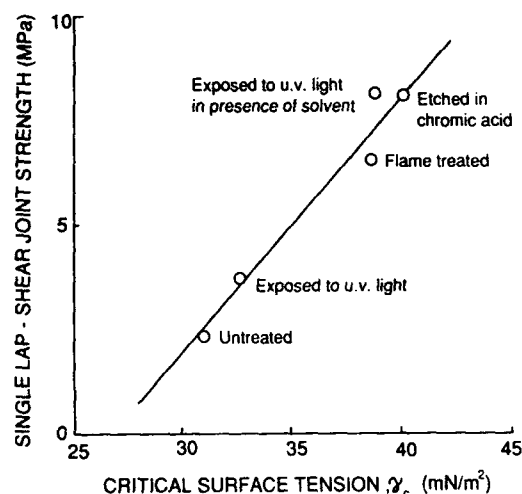CRITICAL SURFACE TENSION γ_c (mN/m²)

Figure 3 Lap shear joint strength for polyethylene pretreated by various methods bonded with an epoxy adhesive. (After Kinloch, ref.5)

In principle, clean metals have much higher surface free energies than polymers (in the vicinity of 1 Jm⁻², commonly). In practice metals are oxidised and have organic contaminants on the surface either as manufacturing processing aids, corrosion protection or from the environment during storage. Thus an effective degreasing procedure is an essential first step for adhesive bonding of metals.

Roughness

The fact that surfaces are not flat on a microscopic level can be exploited. The use of a liquid adhesive which can penetrate the surface roughness, and which subsequently becomes a solid, opens the way for mechanical locking to make a contribution to the strength of the interfacial bonding. Increasing the roughness by some abrasion or etching procedure frequently

forms part of a surface preparation method. Abrasion is also a useful supplement to degreasing for the removed of organic contaminants from metal surfaces.

Specific Surface Layers

In addition to possible surface contamination from the environment, in some instances the chemical composition of the surface region of a solid differs from that of the bulk. In polymers, small molecules of additives, such as plasticisers or antioxidants, may migrate to the surface (bloom) because of incomplete compatibility with the bulk polymer. In polymer samples which have solidified from the melt, especially semi-crystalline polymers, lower molecular weight material tends to be expelled to the surface region. Both these factors lead to a surface region which is weaker than the bulk material. The chromic acid etching of polyethylene prior to bonding removes this weak boundary larger in addition to incorporating more polar groups in the surface[4]. A range of surface preparation methods have been devised for various polymers[6,7].

The nature and role of the oxide surface on metals has received a great deal of attention. By far the greatest effort has been devoted to the study of aluminium and its oxides since this is the most common in the aircraft industry[8]. The rigorous surface pretreatment methods for aluminium adopted for aerospace applications are designed to removed the existing structure and provide another under known conditions and of known properties. A range of specific pretreatment procedures has also been devised for titanium, steel, magnesium and other metals[1,7]. The effects of a rigorous surface preparation procedure on the adhesive bond strength for aluminium are shown in Table 1, by way of illustration of the benefits attainable. Not only is the actual bond strength substantially increased but the variability between replicates is greatly reduced, thereby enhancing confidence. The nature of the surface preparation also has a substantial bearing on bond durability, as discussed later.

Coupling Agents

The bonding of metals frequently includes a layer of a primer, mostly for corrosion inhibiting purposes. What may be regarded as a special type of primer is the coupling agent, commonly a silane. These consist of a range of bifunctional organometallic compounds which possess dual

Table 1 Effect of surface pretreatment on the tensile-shear strength of aluminium-epoxy lap joints.

Surface Pretreatment	Tensile Shear Strength (MPa)	Co-efficient of Variation (%)
As received	3.0	52
Solvent wipe	2.4	
Vapour degrease	5.8	9
Vapour degrease and grit blast	12.1	8
Vapour degrease and chromic acid etch	19.0	1

activity. This permits the metallic end of the molecule to interact with the metal substrate and the organic end to coreact with the adhesive. Thus, by careful choice of the organofunctional moiety a stable bridge is formed at the interface. For example, an amino -or glycidoxy-terminated silane would be used with an epoxy-based adhesive. Other organometallic compounds, most notable titanates, are also used a coupling agents. The concept has been adapted from the fibreglass industry where the use of these compounds as a thin coating at the glass/polymer matrix interface was found to enhance moisture resistance. In adhesive bonding the silane is chosen such that the functional group reacts with the adhesive. In some cases an increased initial strength is also observed. The detailed mode of action of silanes is still disputed and probably depends on the nature of the polysiloxane formed at the interface. Silane coupling agents offer scope as relatively non-toxic, simplified pretreatment methods for metals, while still permitting the formation of strong durable adhesive joints[5,9].

Adhesive and Cohesive Fracture

As pointed out earlier, the object of surface preparation is to avoid interfacial failures in adhesive bonding, that is, to select the level of pretreatment necessary to obviate adhesive (interfacial) failures. Once the failure is cohesive in either the substrate or the adhesive layer use of a more rigorous surface preparation method can cause no further improvement in joint strength.

Identification of the locus of failure, seemingly a straightforward matter, can be difficult as in practice many bonded assemblies contain a number of materials and interfaces. A metal-to-metal joint in which a primer has been employed is shown schematically in Fig. 4. What may at first glance appear an adhesive failure at the

adhesive/primer interface may on closer inspection prove to be a cohesive failure of the metal oxide or an adhesive failure at the primer/oxide interface. Clearly, the true site of the failure must be identified (the weakest link in the assembly) if effective remedial action is to be undertaken.
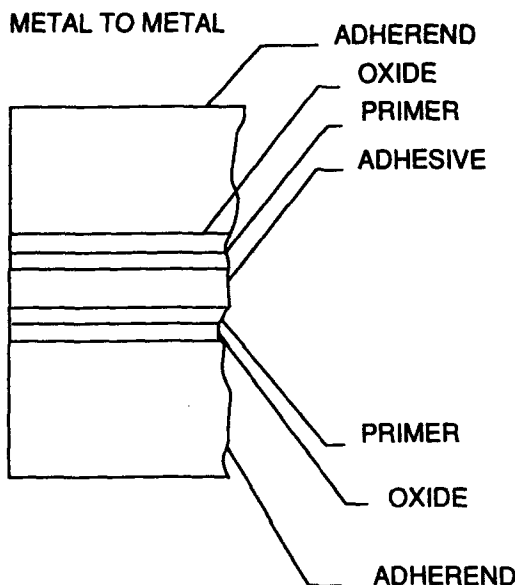
METAL TO METAL

Figure 4   Schematic representation of a metal-to-metal adhesive joint.

JOINT DESIGN

Joint design and the selection of adhesives are closely related topics as the geometry of the joint plays a large part in the type of stress applied to the adhesive (shear, tension, torsion and so on) and thus on the type of adhesive which may be suitable. Special care is needed in the design of joints for dissimilar materials, especially metals to non-metals, as differences in the coefficients of thermal expansion, in particular, can lead to substantial stresses on the adhesive. Special attention to design is needed in the replacement by adhesive bonding in a part previously welded or mechanically fastened. Rarely can a direct substitution be made; rather, the part should be redesigned taking into account the particular requirements for successful adhesive bonding.

Geometric Factors

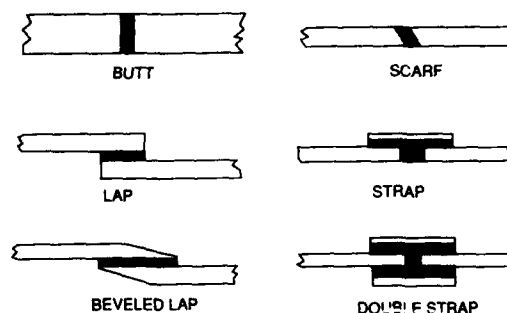Some common joint geometries are shown in Fig. 5.

Figure 5   Some common adhesive joint geometries. (After Schneberger, ref. 12).

Properties of adhesives, quoted on data sheets or in reference books, have been established by experiment using standard (ASTM or other) test methods. These test methods themselves contain various factors which have been extensively studied for the more common test configurations and have an important bearing on the interpretation of adhesive properties and also on the consideration of joint design. The common single lap joint is examined here by way of illustration. This joint configuration is employed to determine the tensile-shear strength of adhesives (ASTM D1002 for metal-to-metal bonds, for example). The standard specimen is 2.5 cm (1.0 in) wide with 1.25 cm (0.5 in) overlap using metal 1.6 mm (0.064 in) thick. Results are quoted as the tensile-shear strength per unit area (MPa or psi).

Two major factors specifically relating to this standard test stand out. Firstly, it has long been established that the stress is by no means uniform over the bonded area being much higher at the ends of the overlap than in the middle (Fig. 6). Secondly, the alignment of the test piece in the testing machine is such that, with high strength adhesives, distortion of the metal substrates can occur which introduces a peel component into the bonded area, most notably at the ends of the overlap[14] (Fig. 7). Thus, for high strength adhesives, the quoted value of the tensile-shear strength may be determined by the much higher than average stresses at the ends of the overlap or the inability of the adhesive to withstand the peel forces at the ends of the overlap. The latter factor is especially important for brittle adhesives, such as unmodified epoxies.

Certain corollaries flow from the above observations which need consideration in adopting the lap joint configuration for a given application. The non-uniform stress distribution means the

notional average stress is not directly proportional to the area bonded. To increase the bond strength an increase in the width of the bonded region is useful but an increase in the overlap length may achieve little, since the ends of the overlap are always a high stress region while the centre section may be virtually unloaded (Fig. 8). The use of thicker or stiffer grades of the substrates reduces the bending moments at the ends of the overlap and thus minimises the peel forces on the adhesive. Alternatively, tapering the substrates at the ends of the overlap, with either an inside or outside taper, significantly reduces the stress concentrations there.
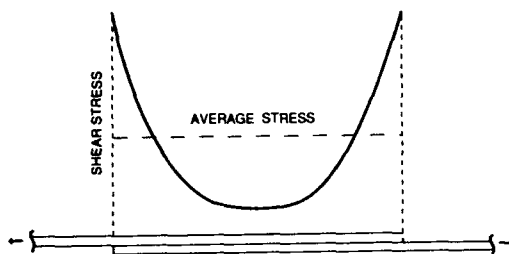

Figure 6   Shear stressed in a lap shear joint. (After Anderson et al., ref 13)
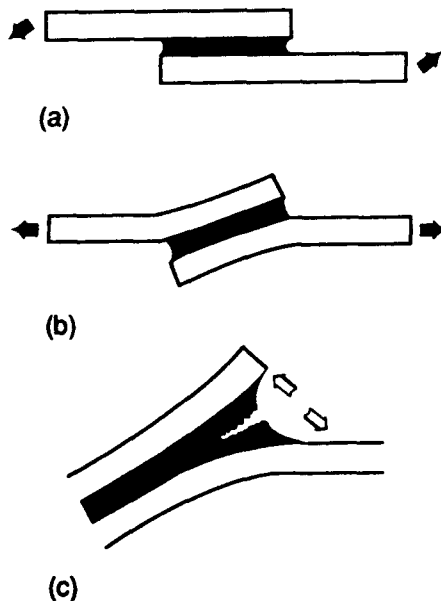

Figure 7   Development of secondary forces during stressing of a lap joint (a) loading is asymmetric, (b) assembly distorts, (c) rupture occurs at the end of an overlap. (After Lees, ref. 14).
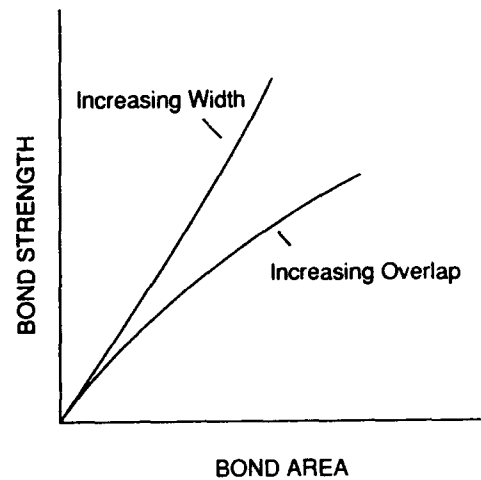

BOND AREA

Figure 8   The effect of overlap length and width on the bond strength of a single lap joint. (After Schneberger, ref. 12).

Adhesive Thickness

Basically it has been shown experimentally that thin bond lines are to be preferred to thick ones, particularly for brittle adhesives[14] and it has been argued that thin bond lines are more durable, especially in fatigue[15]. Variable adhesive thickness is to be avoided if at all possible and thus a means of controlling the thickness is highly desirable. This can be done by the use of shims or the incorporation in the bond line of a small amount of a suitable fibre. Many high strength adhesives for the aircraft industry are supplied supported on a thin fibrous scrim[6].

ADHESIVE SELECTION

A wide range of chemical classes is employed as adhesives. Selection of candidate materials for a particular application depends in large measure on the service operating environment, including the temperature, and the type and level of stress to be encountered. Only a few instances will be considered here, by way of illustration of the trade-offs in properties which may be needed in practice. A number of alternatives may be equally satisfactory as far as the material properties are concerned in a given instance, in which case aspects such as availability and shelf-life may become the deciding factors.

New adhesives are constantly being introduced and the list of those commercially available must

now number many hundreds, if not thousands. A few compilations are available which are useful as a guide to classifications[16,17,18].

Epoxy-Based Systems

Amongst adhesives for structural applications those based on epoxies are widely used in a diversity of specific instances. This arises, in part at least, from the properties of epoxies including low shrinkage on cure, a low level of creep under sustained load, high strength and stiffness, good chemical resistance and good gap-filling qualities. Unmodified epoxies are often brittle and hence impact resistance and peel strength are poor but various modified versions are in common use which significantly improve these properties (Fig. 9). Since epoxies are thermosetting materials, once the substrates are bonded the joint cannot readily be disassembled. Epoxy-based systems have long been used in aircraft applications. These are commonly supplied as one-part films containing latent curing combinations to obviate all problems with correct proportions of the various ingredients and inhomogeneities in mixing. These systems, while convenient to use, have a limited shelf life, typically 6 months at -20°C.
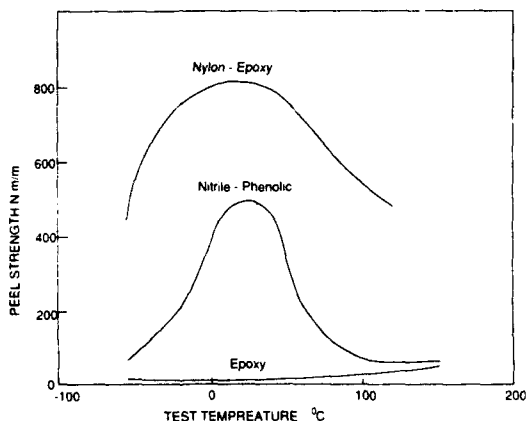

Figure 9 Peel strength of thermoset adhesives as a function of temperature.

For elevated temperature performance it is necessary for the glass transition temperature (Tg) of the adhesive to be higher than the highest temperature to be encountered in service, since above the Tg of any polymer its strength and stiffness diminish rapidly. This means, for thermosetting adhesives generally, that the adhesive must be cured at a temperature higher than that to be subsequently encountered.

Systems designed for high temperature cure (150° C, say) which are only exposed to a much lower temperature (say 80°C) are but partly reacted even though the adhesive has become hard and non-tacky: the cure reaction stopped essentially because the viscosity of the system became too high (vitrification). The Tg would be around 85°-90°C and the strength and stiffness significantly less than the potentially ultimate values. Should the systems subsequently encounter a temperature higher than 80° C the cure reaction would resume pushing the Tg and other physical properties to higher values. It is not at all desirable to rely on the in-service environment for completion of the cure reaction and the establishment of the ultimate adhesive strength properties. In addition, incomplete reaction is undesirable since the presence of reactive, polar groups, such as epoxide moieties, increases the susceptibility to the uptake of moisture and other small molecules to the detriment of long term durability. Incomplete reaction (undercure) is often accompanied by more flexibility in the system since extensive cross linking frequently occurs in the final few percent of the cure reaction. This should not be used as a source of a more flexible adhesive because of the disadvantages outlined above: rather, another adhesive system should be chosen which provides the desired level of flexibility (or peel strength) in its fully reacted state.

Reactive Acrylics

One disadvantage of two-part epoxy systems is that once the resin and curing agent are mixed a fairly short pot life remains in which to affect the assembly. Anaerobics have an advantage in this regard since the two components are not directly mixed but applied one each to the two surfaces to be joined. The free radical vinyl polymerization reaction proceeds in the complete absence of oxygen after the two surfaces have been clamped together. The necessity for no oxygen means thin bond lines are required, that is, the two components to be joined must conform well to each other and repositioning of the components relative to each other after initial contact can weaken the ultimate bond strength. Earlier disadvantages of these systems, such as an unpleasant odour and a certain susceptibility to hydrolysis, have in more recent versions been significantly reduced or eliminated. The Tg of these systems is limited to about 110-120°C.

With an eye to automotive applications, some acrylics have been developed which are tolerant

of oily metal surfaces. The adhesives displace the oil from the metal surface as the adhesive layer spreads and absorb the oil into the bulk of the adhesive layer. However, the same adhesive on a clean metal surface still results in a higher strength for the bonded assembly than on an oily surface (Table 2). Durability is also superior on a rigorously prepared surface.

Table II Adhesive joint strength and surface preparation for an acrylic adhesive

Substrate	Tensile-Shear Strength (MPa)
Steel (solvent wipe)	23
Steel (oily)	20
Aluminium (solvent wipe)	13
Aluminium (acid etch)	28

Manufacturing and Design Factors

Many specific manufacturing, assembly or design factors may play a role in adhesive selection, in addition to the intrinsic properties of the chemical class of the adhesive. That is to say, the adhesive selection cannot be considered in isolation from the particular design or assembly manufacturing process. Thus, for example, for reasons unconnected with the joining process, it may be undesirable to heat an assembly to be bonded, thereby eliminating all elevated temperature curing systems from consideration. A complex shape may prevent the application of sufficient pressure on the bond line during cure thus militating against adhesives which need pressure during cure (phenolics, for example). It may be that after consideration of the requirements for a particular application the best choice would appear to be an epoxy based system but that even a highly toughened epoxy would have inadequate peel strength. It could then be necessary to reconsider the design and the possibilities for change to reduce the peel stress.

DURABILITY

Water is particularly aggressive for adhesive joints and the combination of high temperature and high humidity especially so. Further, high surface free energy substrates (metals) are particularly susceptible to environmental failure in the interfacial region of the joint. Water can displace the adhesive at the interface, hydrolyse the metal oxide structure (thereby weakening it) and hydrolyse the adhesive in the region immediately

adjacent to the interface and hence alter its properties[15,19]. The surface pretreatment can play a substantial role not only in the initial joint strength but also in its durability (Fig 10)[5,20]. The Boeing wedge test was developed to address this point (Fig. 11). A wedge is inserted into the bondline and the assembly aged in a harsh environment (commonly 50°C, 96% RH) and the rate of crack extension measured. Durable bonds show negligible crack growth. The disadvantage of this test method is the difficulty in subjecting the data to a fracture mechanics based analysis; as the crack extends or the substrates deform with time the stress at the crack tip diminishes. It remains, however, a useful screening method.
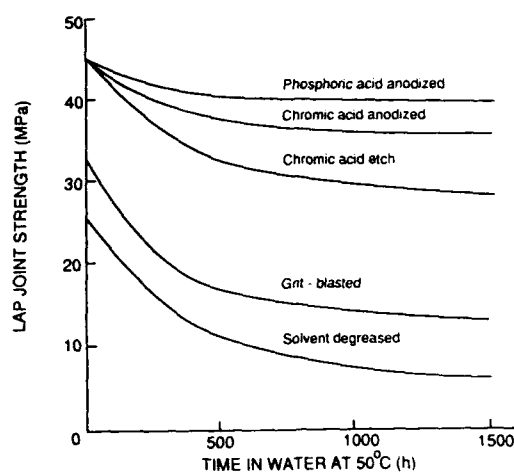

Figure 10 Effect of surface pretreatment on the durability of aluminium alloy/toughened epoxy joints subjected to accelerated aging in water at 50°C. (After Kinloch, ref. 5).

The chemical nature of the adhesive significantly affects the rate and extent of water diffusion through it and the magnitude of the effect of water uptake on the adhesive properties. Nylon-epoxies, for example, while having exceptionally good peel and shear strength and fatigue resistance have very poor moisture resistance: Nitrile-phenolics have good environmental durability even in corrosive salt atmospheres[2,15,19,20].

The loss of adhesive joint strength due to environmental factors can be significantly accelerated by the presence of a stress[2,21] (Fig. 12.). Adhesive selection based on exposure trials of unstressed joints has led to optimistic expectations of the lifetime for stressed bonded structures. Trials should simulate the anticipated service conditions, if possible.
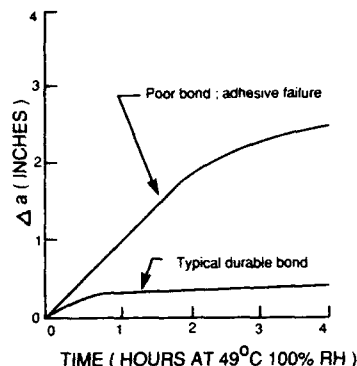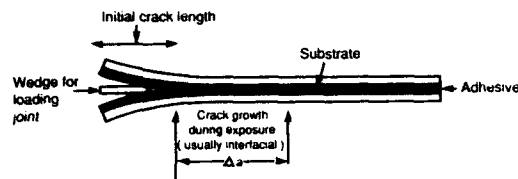
Figure 11 The wedge test for assessment of bond durability. (After McMillan, ref. 21).
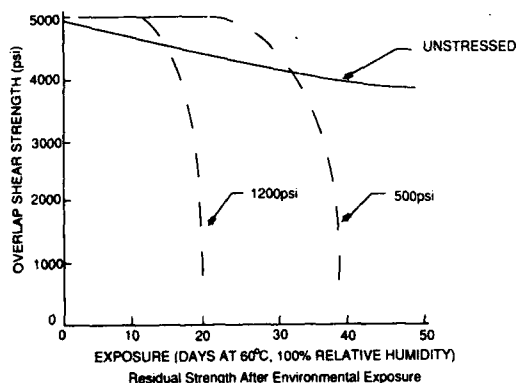

Figure 12 Effect of stress on the durability of aluminium/epoxy lap joints. (After McMillan, ref. 21).

SUMMARY

The benefits to be gained from the use of adhesive bonding as a method of joining are substantial and include such aspects as a uniform stress distribution and weight savings. However, to realise the potential benefits considerable attention needs to be paid to a number of factors. The surface preparation needs to be tailored for the materials to be joined, the type and level of stresses and the operating environment to be encountered in service. These factors must also be considered in the selection of the adhesive chemical class. Much is now known about these factors and the interactions between them so that appropriate choices can be made and thus strong, durable bonding can be achieved.

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